

ZAVALÍAITE, $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})_3(\text{PO}_4)_2$, A NEW MEMBER OF THE SARCOPSIDE GROUP FROM THE LA EMLEADA PEGMATITE, SAN LUIS PROVINCE, ARGENTINA

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ABSTRACT

Zavalíaite, $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})_3(\text{PO}_4)_2$, belongs to the sarcopside group of minerals and corresponds to the Mn^{2+} equivalent of sarcopside and chopinite. It occurs at the La Emleada pegmatite, San Luis Province, Argentina. Zavalíaite forms colorless and transparent exsolution-lamellae up to 70 μm thick and 1.5 mm long in lithiophilite. Owing to hydration, the mineral partially hydrates to reddingite, $(\text{Mn}^{2+}, \text{Fe}^{2+})_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. Lamellae of zavalíaite display a perfect cleavage along the $\{100\}$ or $\{001\}$ direction. The luster is vitreous to resinous, and the streak is white. Optically, the mineral is biaxial (–), with an average index of refraction of 1.66(1) (for $\lambda = 589$ nm), $2V_{\text{meas}} = 15(5)^\circ$. It is non-pleochroic, without dispersion; the cleavage plane shows an angle of ca. 45° with the elongation of the lamellae; X is perpendicular to this cleavage plane. Zavalíaite is non-fluorescent under short-wave and long-wave ultraviolet light, and its calculated density is 3.68 g/cm³. The mineral is brittle, with a Mohs hardness of 4. The mean chemical composition, determined with an electron microprobe from 27 point analyses (wt.%), is: P_2O_5 41.38, FeO 24.94, MgO 6.09, MnO 27.08, total 99.49. The empirical formula, calculated on the basis of eight atoms of oxygen per formula unit, is $(\text{Mn}^{2+}_{1.31}\text{Fe}^{2+}_{1.19}\text{Mg}_{0.52})_{\Sigma 3.02}(\text{P}_{1.00}\text{O}_4)_2$. Zavalíaite is monoclinic, space group $P2_1/c$, a 6.088(1), b 4.814(1), c 10.484(2) Å, β 89.42(3)°, V 307.2(1) Å³, and $Z = 2$. The crystal structure is identical to that of sarcopside and chopinite, with the $M1$ site occupied by 0.5 $\text{Fe}^{2+} + 0.35\text{Mn}^{2+} + 0.15$ Mg, and the $M2$ site occupied by 0.475 $\text{Mn}^{2+} + 0.35$ $\text{Fe}^{2+} + 0.175$ Mg. The strongest eight lines in the X-ray powder pattern [d in Å (intensities estimated visually) (hkl)] are: 6.75 (very strong) (100), 3.54 (weak) (012)(11 $\bar{1}$), 2.964 (strong) (200), 2.816 (weak) (013), 2.537 (strong) (11 $\bar{3}$), 1.894 (very strong) (220), 1.848 (very strong) (311), and 1.652 (very strong) (313)(31 $\bar{3}$). The mineral has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association [IMA 2011–012], and is named in honor of María Florencia de Fátima Márquez Zavalía [or Márquez-Zavalía], investigator of Argentinian minerals and ore assemblages and Head of the Department of Mineralogy, Petrography and Geochemistry, IANIGLA, CCT Mendoza, CONICET (National Research Council of Argentina).

Keywords: zavalíaite, new phosphate mineral species, sarcopside group, granitic pegmatites, San Luis, Argentina.

SOMMAIRE

La zavalíaite, $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})_3(\text{PO}_4)_2$, nouvelle espèce de phosphate, appartient au groupe du sarcopside, et correspond à l'équivalent manganésifère du sarcopside et de la chopinite. Le minéral a été trouvé dans la pegmatite de La Emleada, province de San Luis, Argentine. La zavalíaite forme des domaines exsolvés transparents et incolores atteignant 70 μm d'épaisseur et 1,5 mm de longueur, inclus dans la lithiophilite. L'hydratation de ce minéral produit la reddingite, $(\text{Mn}^{2+}, \text{Fe}^{2+})_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$.

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Les lamelles de zavalfaïte montrent un clivage parfait selon {100} ou {001}; l'éclat est vitreux à résineux, et la rayure est blanche. Optiquement, le minéral est biaxe négatif et montre un indice de réfraction moyen de 1,66(1) (pour $\lambda = 589$ nm), pour un angle $2V_{\text{mesuré}}$ de $15(5)^\circ$. Aucun pléochroïsme n'a été observé, ainsi qu'aucune dispersion; le plan de clivage montre un angle d'approximativement 45° avec l'allongement des lamelles d'exsolution, et X est perpendiculaire à ce plan de clivage. La zavalfaïte n'est pas fluorescente. Sa densité calculée est $3,68 \text{ g/cm}^3$. Le minéral est cassant, et sa dureté Mohs est 4. La composition chimique moyenne, déterminée avec une microsonde électronique à partir de 27 analyses ponctuelles, correspond (% en poids) à: P_2O_5 41,38, FeO 24,94, MgO 6,09, MnO 27,08, total 99,49. La formule empirique, calculée sur la base de huit atomes d'oxygène, est $(\text{Mn}^{2+}_{1,31}\text{Fe}^{2+}_{1,19}\text{Mg}_{0,52})_{\Sigma 3,02}(\text{P}_{1,00}\text{O}_4)_2$. La zavalfaïte est monoclinique, groupe spatial $P2_1/c$, a 6,088(1), b 4,814(1), c 10,484(2) Å, β 89,42(3)°, $V = 307,2(1) \text{ Å}^3$, et $Z = 2$. Le minéral présente une structure identique à celles du sarcopside et de la chopinite, avec le site M1 occupé par $0,5 \text{ Fe}^{2+} + 0,35\text{Mn}^{2+} + 0,15 \text{ Mg}$, et le site M2 occupé par $0,475 \text{ Mn}^{2+} + 0,35 \text{ Fe}^{2+} + 0,175 \text{ Mg}$. Les huit réflexions les plus intenses du diffractogramme de poudres de rayons X sont [d en Å (intensités estimées visuellement) (hkl): 6,75 (très fort) (100), 3,54 (faible) (012)(11 $\bar{1}$), 2,964 (fort) (200), 2,816 (faible) (013), 2,537 (fort) (11 $\bar{3}$), 1,894 (très fort) (220), 1,848 (très fort) (311), et 1,652 (très fort) (313)(31 $\bar{3}$). Le minéral a été approuvé par la "Commission on New Minerals and Mineral Names of the International Mineralogical Association" sous le numéro IMA 2011–012; il est nommé en l'honneur de María Florencia de Fátima Márquez Zavalía (ou Márquez-Zavalía), chercheur et responsable du Département de Minéralogie, Pétrographie et Géochimie, IANIGLA, CCT Mendoza, CONICET (Conseil de Recherche National, Argentine).

Mots-clés: zavalfaïte, nouveau phosphate, groupe du sarcopside, pegmatites granitiques, San Luis, Argentine.

INTRODUCTION

In the northeastern part of the San Luis Range, Argentina, granitic pegmatites are common. Many of them are enriched in phosphorus and commonly show phosphate nodules (Hurlbut & Aristarain 1968, Oyarzábal & Galliski 2007, Galliski *et al.* 2009, Roda-Robles *et al.* 2009). During a field trip organized by Dr. Miguel Galliski in 2008, several pegmatites of this region were visited. One of them, the La Empleada pegmatite, hosts large nodules of lithiophilite [$\text{Li}(\text{Mn}^{2+}, \text{Fe}^{2+})\text{PO}_4$]. Several of these samples were collected, and an examination of thin sections under the polarizing microscope showed the presence of exsolution lamellae in lithiophilite.

Electron-microprobe analysis of these lamellae showed them to be the Mn^{2+} analogue of sarcopside [$(\text{Fe}^{2+}, \text{Mn}^{2+})_3(\text{PO}_4)_2$]. In this paper, we report the description of this new phosphate mineral, $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})_3(\text{PO}_4)_2$, which has been approved by the CNMNC–IMA (IMA 2011–012; Hatert *et al.* 2011) and named *zavalfaïte* in honor of María Florencia de Fátima Márquez Zavalía (or Márquez-Zavalía) (born 1955), researcher and Head of the Department of Mineralogy, Petrography and Geochemistry, IANIGLA, CCT Mendoza, CONICET (National Research Council of Argentina). She has contributed to our knowledge of Argentinian mineralogy, from pegmatitic to hydrothermal ore minerals, participating in the study of new species such as ferrotitanowodginite, other wodginite-group minerals, bismutotantalite, and numerous phosphate minerals from granitic pegmatites. The holotype sample of zavalfaïte is deposited in the collections of the Laboratory of Mineralogy, University of Liège, catalogue number 20384.

GEOLOGICAL SETTING

Zavalfaïte occurs in the La Empleada granitic pegmatite of the Totoral pegmatite field, located in the southern part of the San Luis Range in the Sierras Pampeanas Orientales of northwestern Argentina. It is located at $32^\circ 53' 38.26''$ S and $65^\circ 55' 50.5''$ W (1363 m above sea level). The geology of the area is as described by Galliski *et al.* (2009) for the Santa Ana pegmatite. It consists of a thick folded psammopelitic sequence belonging to the Pringles Metamorphic Complex, of Cambrian to Ordovician age (Sims *et al.* 1997, Steenken *et al.* 2006). This sequence was intruded by a suite of Ordovician leucogranites and a swarm of genetically linked granitic pegmatites of LCT (Li–Cs–Ta) signature (Oyarzábal *et al.* 2009). The northern intrusive body of this suite is known as the Cerro La Torre pegmatitic granite. East of this granite, a group of pegmatites belonging to the beryl–columbite–phosphate subtype, rare-element subclass (according to Černý & Ercit 2005) has been mapped, in which the Santa Ana and La Empleada pegmatites are representative units.

Both pegmatites outcrop approximately 1000 m to the east of the Cerro La Torre granite on both sides of the La Viborita creek (Fig. 1). The southern mine is called La Empleada and consists of four pegmatites in a medium-grade dark-grey micaschist with a quartz + muscovite + biotite + plagioclase + almandine + cordierite \pm (sillimanite) assemblage that contains dispersed centimeter-sized nodules of altered cordierite. Most of these pegmatites strike N–S and are subvertical, but to the East, the last two bodies deviate to the northwest and dip to southwest at a high angle. The pegmatite was initially mined for beryl, and later on for muscovite, K-feldspar and quartz. Today, the quarries are inactive.

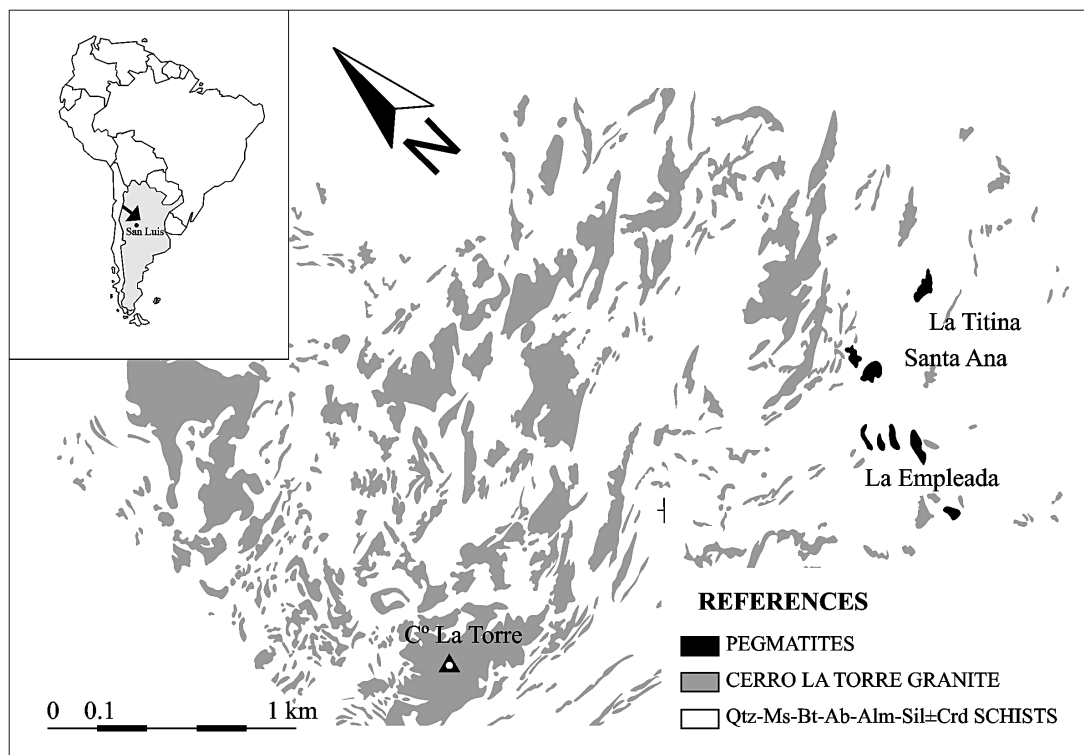


FIG. 1. Schematic map showing the location of the La Empleada pegmatite, with the simplified geology of the Santa Ana pegmatite group, modified from Galliski *et al.* (2009).

The pattern of zoning is similar in all the bodies and consists of border, wall, intermediate and core zones. The border zone is 4–8 cm wide, fine grained and shows the assemblage Qtz–Ab–Kfs–Ms±Tur–Ap. The wall zone shows a larger grain-size and similar mineralogy except for tourmaline, which is almost absent. The intermediate zone is formed of giant K-feldspar crystals in a coarse-grained interstitial matrix of quartz, albite and muscovite; inward, it grades into a quartz core. Giant crystals of K-feldspar commonly are replaced by a fine-grained association of albite + muscovite, with subordinate quartz. The pegmatites and the host rock show evidence of post-emplacement deformation.

In the core–margin association of the three eastern pegmatites, we found nodules of primary phosphates and scarce crystals of beryl. The size of the phosphate nodules varies from 0.5 to 1.2 m. They are usually ellipsoidal, dark brown to black, with a fractured surface surrounded by cm-wide milky quartz that grades inward to an irregular border of muscovite flakes with a dull green stain of secondary phosphates, possibly mitridatite. Inward, the nodules have a cap of variable thickness of dark manganese oxides that are irregularly distributed.

APPEARANCE AND PHYSICAL PROPERTIES

Zavaláite forms colorless and transparent exsolution lamellae up to 70 μm thick and 1.5 mm long, included in lithiophilite. In crossed polars, zavaláite lamellae show high interference-colors compared to lithiophilite (Fig. 2). The mineral partially hydrates to reddingite, $(\text{Mn}^{2+}, \text{Fe}^{2+})_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, which shows a more brownish color. Lamellae of zavaláite display a perfect cleavage along the $\{100\}$ or $\{001\}$ direction, as observed in thin section. The mineral is brittle, and its Mohs hardness is *ca.* 4, estimated by comparison with other minerals of the sarcopside group. The luster is vitreous to resinous, and the streak is white. Zavaláite is biaxial (–), with an average index of refraction of 1.66(1) (for $\lambda = 589 \text{ nm}$), $2V_{\text{meas}} = 15(5)^\circ$. The mineral is non-pleochroic, without any dispersion; the cleavage plane shows an angle of *ca.* 45° with the elongation of the lamellae; X is perpendicular to this cleavage plane. Zavaláite is non-fluorescent under short-wave (254 nm) and long-wave (366 nm) ultraviolet light. Owing to the small grain-size, the density was not measured directly; the density calculated from the empirical formula and single-crystal data is 3.68 g/cm^3 . The compatibility



FIG. 2. Lamellae of zavaláite included in lithiophilite, La Empleada pegmatite, San Luis, Argentina (crossed polars, field of view 2.5 mm).

TABLE 1. THE COMPOSITION OF ZAVALÁITE

	wt. %	Range	Stand. dev.	Empirical formula ^a	
P ₂ O ₅	41.38	40.56 – 42.19	0.44	P <i>apfu</i>	1.995
FeO	24.94	23.44 – 25.82	0.52	Fe ²⁺	1.188
MgO	6.09	5.78 – 6.31	0.16	Mg	0.517
MnO	27.08	24.90 – 28.37	0.63	Mn ²⁺	1.307
Total	99.49				

The composition quoted is the average results of 27 electron-microprobe analyses. ^a Calculated on the basis of eight atoms of oxygen per formula unit (*apfu*).

index, deduced from this calculated density, is $1 - (K_P/K_C) = 0.052$, which correspond to the “good” category (Mandarino 1981).

CHEMICAL COMPOSITION

Quantitative chemical analyses were done on a polished thin section using a Cameca SX-50 electron microprobe operating in wavelength-dispersive mode, and located at the Université de Toulouse, France. The accelerating voltage was 15 kV, with a beam current of 10 nA, a spot size of 3 μm, and a count time of 10 s on the peaks and 5 s on the backgrounds. Natural minerals were used as standards: graptone for P, periclase for Mg, hematite for Fe, and pyrophanite for Mn. The raw

data were corrected for matrix effects using the PAP method (Pouchou & Pichoir 1984).

The mean analytical results (average of 27 point analyses) are reported in Table 1. Neither H₂O nor CO₂ could be determined directly because of the small amount of material; in any case, these groups are absent from the mineral, as shown by the structural results (see below). Aluminum, Ca, Na, K, and Cl are below detection limits. The empirical formula was calculated on the basis of eight atoms of oxygen per formula unit: $(Mn^{2+}_{1.31}Fe^{2+}_{1.19}Mg_{0.52})_{\Sigma 3.02}(P_{1.00}O_4)_2$. The simplified formula is $(Mn^{2+}, Fe^{2+}, Mg)_3(PO_4)_2$, which requires: MnO 26.90 wt.%, FeO 25.34%, MgO 6.04%, P₂O₅ 41.72%, for Mn:Fe:Mg proportions of 0.43:0.40:0.17, with a total of 100.00 wt.%.

X-RAY-DIFFRACTION DATA AND CRYSTAL-STRUCTURE REFINEMENT

The sarcopside-type structure of zavaláite was first confirmed by X-ray powder diffraction using a Debye-Scherrer camera (diameter 114.6 mm, CuKα radiation); the corresponding X-ray powder-diffraction pattern (Table 2) was used to calculate the unit-cell parameters with the LCLSQ software (Burnham 1991): *a* 6.13(1), *b* 4.80(1), *c* 10.38(4) Å, β 89.9(2)°, *V* 305.4(9) Å³ (*Z* = 2, space group *P2₁/c*). The X-ray structural study of zavaláite was done on an Oxford Diffraction Gemini PX Ultra four-circle diffractometer equipped with a Ruby CCD area-detector (FUNDP, Namur, Belgium) on

a crystal fragment measuring $0.04 \times 0.05 \times 0.10$ mm. In all, 198 frames with a spatial resolution of 1° were collected by the ϕ/ω scan technique, with a count time of 10 s per frame, in the range $6.70 < 2\theta < 58.34^\circ$. In all, 1477 reflections were extracted from these frames, corresponding to 724 unique reflections. Unit-cell parameters refined from these reflections are a 6.088(1), b 4.814(1), c 10.484(2) Å, β 89.42(3)°, V 307.2(1) Å³, in good agreement with those refined from the powder-diffraction data. The data were corrected for Lorenz, polarization and absorption effects, the latter with an empirical method using the SCALE3 ABSPACK scaling algorithm included in the CrysAlisRED package (Oxford Diffraction 2007).

The crystal structure of zavaláite (Fig. 3) was refined with SHELXTL (Sheldrick 2008) in space group $P2_1/c$, starting from the atom coordinates of chopinite (Grew *et al.* 2007); scattering curves for neutral atoms, together with anomalous-dispersion corrections, were

taken from the International Tables for X-ray Crystallography (Wilson 1992). The relative occupancies of Fe²⁺ and Mg at $M1$, and of Mn²⁺ and Mg at $M2$, were refined. The refinements were completed using anisotropic-displacement parameters for all atoms. The final conventional R_1 factor [$F_0 > 2\sigma(F)$] is 0.0383; further details on the intensity-data collection and structure refinement are given in Table 3. A table of structure factors is available from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document Zavaláite CM50_1445].

The crystal structure of zavaláite is identical to those of sarcopside (Moore 1972) and chopinite (Grew *et al.* 2007), and can be compared to the structure of olivine in which Si⁴⁺ is replaced by P⁵⁺. The consequences of this substitution are the presence of vacancies at one-third of the $M1$ sites (Fig. 3), as well as strong distortions of octahedra induced by bond-valence requirements. These distortions have induced a marked ordering of Fe²⁺ at the $M1$ site, and of Mn²⁺

TABLE 2. X-RAY POWDER-DIFFRACTION PATTERN OF ZAVALÁITE

I_{obs}	d_{obs} (Å)	I_{calc}	d_{calc} (Å)	hkl
vs	6.75	58	6.126	1 0 0
vw	4.93	3	5.190	0 0 2
vw	4.15	20	4.359	0 1 1
w	3.54	100	3.538	1 1 $\bar{1}$, 0 1 2
s	2.964	38	3.063	2 0 0
w	2.816	81	2.808	0 1 3
s	2.537	20	2.550	1 1 $\bar{3}$
w	2.317	9	2.314	2 1 2
vs	1.894	6	1.890	2 2 0
vs	1.848	20	1.850	3 1 1
w	1.774	53	1.776	2 2 2, 2 2 $\bar{2}$
vs	1.652	27	1.652	3 1 3, 3 1 $\bar{3}$

Intensities were estimated visually (vs: very strong, s: strong, w: weak, vw: very weak). The strongest eight lines are in bold. The calculated intensities were derived from the structural data with the SHELXTL-XPOW software (Sheldrick 1990). Calculated values of d were acquired with the software LCLSQ (Burnham 1991) from the unit-cell parameters a 6.13(1), b 4.80(1), c 10.38(4) Å, β 89.9(2)°.

TABLE 3. EXPERIMENTAL DETAILS FOR THE SINGLE-CRYSTAL X-RAY-DIFFRACTION STUDY OF ZAVALÁITE

Color	grey
Dimensions of the crystal (mm)	ca. $0.04 \times 0.05 \times 0.10$
a, b, c (Å)	6.088(1), 4.814(2), 10.484(2)
β (°)	89.42(3)
V (Å ³)	307.2(1)
Space group	$P2_1/c$
Z	2
$2\theta_{\text{min}}, 2\theta_{\text{max}}$	$6.70^\circ, 58.34^\circ$
Range of indices	$-6 \leq h \leq 7, -6 \leq k \leq 5, -10 \leq l \leq 14$
Measured intensities	1477
Unique reflections	724
Independent non-zero reflections	609
$[I > 2\sigma(I)]$	
μ (mm ⁻¹)	5.977
Refined parameters	65
R_1 [$F_o > 2\sigma(F)$]	0.0383
R_1 (all)	0.0484
wR_2 (all)	0.1255
S (goodness of fit)	0.891
Max Δ/σ in the last I.s. cycle	0.000
Max peak and hole in the final ΔF map (e/Å ³)	+0.75 and -0.70

TABLE 4. FINAL FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS (Å²) OF ATOMS IN ZAVALÁITE

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
$M1^*$	0.5	0	0.5	0.0124(6)	0.0071(6)	0.0091(6)	0.0001(4)	-0.0021(4)	0.0005(3)	0.0095(4)
$M2^{**}$	0.2641(1)	0.0129(2)	0.78228(7)	0.0102(5)	0.0105(5)	0.0083(5)	-0.0005(3)	-0.0002(3)	0.0001(3)	0.0096(3)
P	0.2389(2)	-0.4317(3)	0.5996(1)	0.0091(6)	0.0068(6)	0.0080(6)	-0.0004(5)	-0.0012(4)	0.0004(4)	0.0080(4)
O1	0.2183(5)	0.2519(7)	0.6044(3)	0.013(2)	0.009(2)	0.011(2)	-0.001(1)	-0.001(1)	-0.000(1)	0.0108(7)
O2	0.2468(5)	-0.3174(7)	0.4630(3)	0.016(2)	0.013(2)	0.006(2)	-0.001(1)	-0.001(1)	0.000(1)	0.0117(7)
O3	0.0325(5)	-0.2822(7)	0.6604(3)	0.012(2)	0.008(2)	0.012(2)	-0.001(1)	0.003(1)	0.000(1)	0.0104(7)
O4	0.5699(5)	0.3262(7)	0.3193(3)	0.012(2)	0.012(2)	0.012(2)	-0.004(1)	-0.004(1)	0.000(1)	0.0122(7)

Occupancy factors : * 0.85(1) Fe²⁺ + 0.15(1) Mg; ** 0.83(1) Mn²⁺ + 0.17(1) Mg.

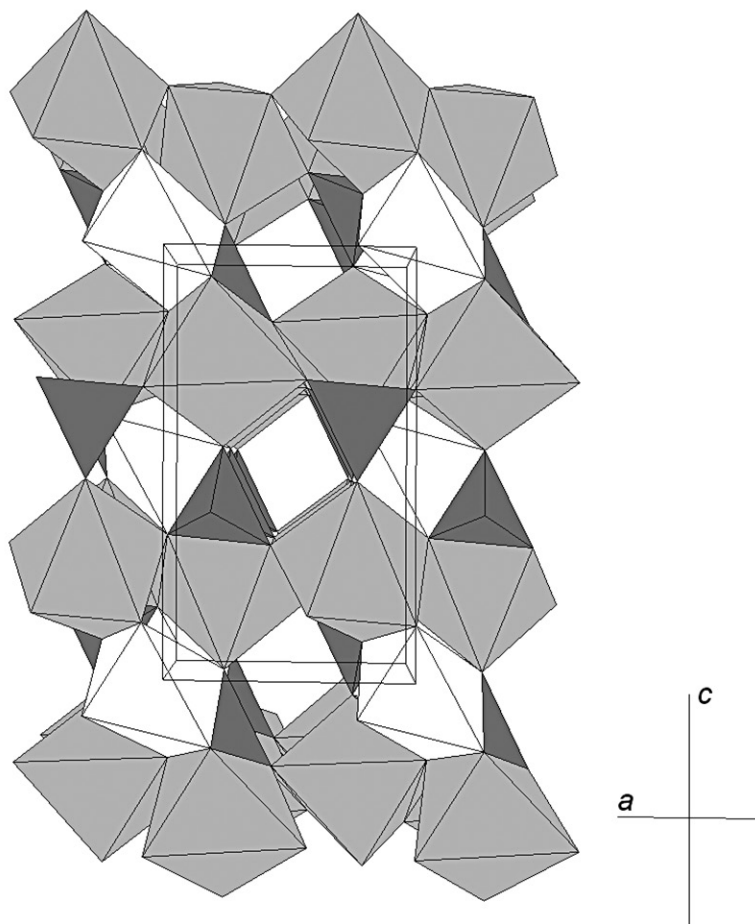


FIG. 3. The crystal structure of zavaláite, projected along the *b* axis. The *M1* octahedra are shown in white, and the *M2* octahedra are shown in light grey, with the *PO*₄ tetrahedra in dark grey.

TABLE 5. SELECTED BOND-DISTANCES (Å) AND ANGLES (°) IN ZAVALÁITE

<i>M1</i> -O1 × 2	2.113(3)	P-O1	1.529(3)
<i>M1</i> -O3 × 2	2.173(3)	P-O2	1.534(3)
<i>M1</i> -O2 × 2	2.175(3)	P-O3	1.577(3)
Mean	2.154	P-O4	1.535(3)
		Mean	1.544
<i>M2</i> -O4	2.057(3)	O1-P-O2	112.9(2)
<i>M2</i> -O2	2.117(3)	O1-P-O3	112.1(2)
<i>M2</i> -O3	2.139(3)	O2-P-O3	103.4(2)
<i>M2</i> -O4'	2.191(3)	O1-P-O4	112.0(2)
<i>M2</i> -O1	2.211(3)	O2-P-O4	112.4(2)
<i>M2</i> -O3'	2.382(3)	O3-P-O4	103.3(2)
Mean	2.183	Mean	109.35

at the *M2* site (Table 4). The dominance of Mn²⁺ at the *M2* site explains the long <*M2*-O> distance, 2.183 Å, compared to the shorter <*M1*-O> bond distance, 2.154 Å (Table 5). The final occupancies are as follows: *M1*: 0.5 Fe²⁺ + 0.35Mn²⁺ + 0.15 Mg; *M2*: 0.475 Mn²⁺ + 0.35 Fe²⁺ + 0.175 Mg. Bond-valence calculations with the empirical parameters of Brown & Altermatt (1985) indicate bond-valence sums of 2.01 at *M1*, 1.95 at *M2*, 4.88 at *P* and 1.93–1.99 for the O atoms, in good agreement with the expected values.

DISCUSSION

Zavaláite belongs to the sarcopside group of minerals (Strunz 8.AB.15, Dana 38.3.1.1.); as in

sarcopsidite and chopinitite, both *M1* and *M2* sites are here considered together for nomenclature purposes (Hatert & Burke 2008). Even if the *M1* site is occupied mainly by Fe²⁺ (Table 4), the total Mn²⁺ content of the mineral is higher than its Fe²⁺ content. Consequently, zavaláite is the Mn²⁺ analogue of sarcopsidite. The same situation occurs in chopinitite, where the *M1* site is occupied mainly by Fe²⁺ (0.518 Fe²⁺ + 0.482 Mg), whereas the *M2* site is occupied mainly by Mg (0.893 Mg + 0.107 Fe²⁺), with a total Mg content higher than the Fe²⁺ content (Grew *et al.* 2007). A comparison of the physical properties of zavaláite, sarcopsidite and chopinitite is shown in Table 6.

As observed in Figure 2, zavaláite forms exsolution lamellae within lithiophilite. Exsolution occurred during the cooling of primary Li-poor lithiophilite; consequently, zavaláite can be considered as a primary phosphate mineral that crystallized under conditions of pegmatite crystallization similar to those of lithiophilite formation. Starting from the proportions of zavaláite in the exsolution textures (less than 10% zavaláite), and using the experimental triphylite–sarcopsidite geothermometer described by Hatert *et al.* (2009), a temperature of *ca.* 300°C can be estimated for the crystallization of zavaláite. This temperature is in fairly good agreement with those occurring in such lithiophi-

lite-rich evolved pegmatites as the Tanco pegmatite, in Manitoba, Canada, in which fluid-inclusion microthermometric measurements indicate temperatures of *ca.* 450°C (London 1986, Morgan & London 1987).

ACKNOWLEDGMENTS

This paper is dedicated to Peter Černý, in recognition of his outstanding contributions to the mineralogy and petrography of granitic pegmatites. Many thanks are due to Olaf Medenbach for the measurement of the optical properties of zavaláite, to F.C. Hawthorne and D. Atencio for their constructive reviews, as well as to R.F. Martin for his editorial help. Frédéric Hatert thanks the FRS–F.N.R.S. (Belgium) for a position of “Chercheur qualifié”.

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TABLE 6. COMPARISON OF THE PHYSICAL PROPERTIES OF MINERALS OF THE SARCOPSIDE GROUP

Mineral	Sarcopsidite	Chopinitite	Zavaláite
Ideal formula	(Fe ²⁺ ,Mn,Mg) ₃ (PO ₄) ₂	(Mg,Fe) ₃ (PO ₄) ₂	(Mn,Fe ²⁺ ,Mg) ₃ (PO ₄) ₂
Space group	<i>P2₁/a</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	10.44(2)	5.9305(7)	6.088(1)
<i>b</i> (Å)	4.768(9)	4.7583(6)	4.814(1)
<i>c</i> (Å)	6.026(8)	10.257(1)	10.484(2)
β (°)	90.0(2)	90.663(9)	89.42(3)
<i>Z</i>	2	2	2
Strong X-ray lines	6.06(50) 3.94(80) 3.54(100) 3.03(40) 2.82(70) 2.57(70) 2.49(50) - - 1.771(40)	5.92(42) 3.84(100) 3.48(52) - - 2.51(72) 2.44(73) - - -	6.75(58) - 3.54(100) 2.964(38) 2.816(81) 2.537(20) - 1.894(6) 1.848(20) 1.774(53) 1.652(27)
Cleavage	{100}, {001} good; {010} poor	-	{100} or {001} good
Density	3.79	3.34 (calc.)	3.68 (calc.)
Optical sign	B(-)	B(-)	B(-)
2 <i>V</i> (°)	27(1)	40(2)	15(5)
α	1.673(3)	1.595(2)	-
β	1.729(1)	1.648(2)	} 1.66(1)
γ	1.732(2)	1.656(2)	
Hardness	4	-	4
Color	Pink, brown to grey, colorless	Colorless	Grey, bluish, colorless
References	[1, 2, 3, 4]	[5]	This work

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Received October 12, 2012, revised manuscript accepted November 19, 2012.